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CYCLONE-ELECTROTHERMAL METHODS OF PROCESSING COPPER AND POLYMETALLIC MATERIALS: EFFECT OF PARTIAL PRESSURE OF SULFUR DIOXIDE ON THE TRANSFER OF COPPER INTO SLAG IN THE COPPER - SLAG - SULFUR DIOXIDE SYSTEM

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CYCLONE-ELECTROTHERMAL METHODS OF PROCESSING COPPER AND POLYMETALLIC MATERIALS

[Tsiklonno-elektrotermicheskiye sposoby pererabotki mednogo i polimetallicheskogo syr'ya]

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This volume contains articles summarizing the results of investigations of processing the copper and polymetallic concentrates and other products of nonferrous metallurgy by the cyclone method. The results of theoretical studies of the technology of cyclone smelting of sulfide concentrates are also included. Certain structural features of a cyclone facility for direct-flow and separated outflow of the smelting products and of gas are described. Also, technological characteristics are given for smelting of copper concentrates of Central Kazakhstan, industrial concentration products of the lead-zinc ores, and oxidized materials.

The material in this volume will be of interest to scientists, workers in metallurgical plants who investigate methods of processing sulfide concentrates in pulverized form, and to instructors and students in the institutions of higher learning.

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EFFECT OF PARTIAL PRESSURE OF SULFUR DIOXIDE ON THE TRANSFER OF COPPER INTO SLAG IN THE COPPER - SLAG - SULFUR DIOXIDE SYSTEM

Z.T. Shaukenbayeva, A.N. Kviatkovskiy, I.A. Onayev and V.N. Galuzo

In the processing of copper concentrates, the existing methods employed for producing a crude copper material involve two independent reduction steps: smelting in a reverberatory, shaft or electrothermal furnace into a matte, and then conversion of the obtained matte into blister copper. In these methods, the relatively rich in copper converter slags, which amount to 25-40% of the weight of the initial concentrate, are poured back into the reverberatory furnace for additional recovery of copper.

In recent years, methods are beginning to be developed in which it is attempted to combine these two reduction steps in one smelting assembly, in particular — in a cyclone furnace, directly producing blister copper. Preliminary experiments have shown that during processing of copper concentrates in a cyclone furnace the operations of melting and oxidation of iron sulfide and its transfer into the slag, and, finally, the oxidation of copper sulfide into the crude metal are achieved in one stage. However, under these conditions the output of slag which is rich in copper (2-5%) is higher here than in usual smelting [1]. This feature proves to be one of the basic shortcomings of the cyclone method. However, it is not impossible that this shortcoming can be eliminated by either the application of more economical ways of processing the slags, or the provision of conditions under which we obtain a slag which is poor in copper.

It was shown in a previous work [1, 2] that, in the cyclone smelting of the concentrate into blister copper, the presence of free oxygen in the gaseous phase leads to peroxidation of the slag, which is moreover, the reason for the appearance of the oxidized compounds of copper in the slag.

At the present level of development of technology, we can more or less accurately regulate the consumption of oxygen and of the concentrate. If we use, say, technical-grade oxygen in the role of the blow gas, the smelting may proceed autogeneously with the production of a gas containing a high concentration of sulfur dioxide (80-90% SO_2). In this case, the content of copper in oxidized form in the slag will be determined solely by the partial pressure of sulfur dioxide in the gaseous phase. A quantitative estimate of the content of copper oxide in the slag is impossible, since we have no data on the activity of copper in matte and metallic phases, jointly present in the melt. In addition, it is not clear whether we can obtain blister copper without the additional formation of the matte phase, with a large content of SO_2 in the gaseous phase. In this connection, we describe in this paper the results of investigations aimed at clarifying these relationships in the copper - slag - P_{SO_2} system. In these experiments we varied P_{SO_2} and the slag composition.

For the initial materials, we utilized synthetic slags, prepared from chemically pure oxides by melting in graphite-fireclay crucibles. To remove the metallic iron and magnetite from the slags, the latter were ground and subjected to the magnetic separation. The chemical analysis of the prepared slags is presented in Table 1.

The experiments were conducted at a temperature of 1250°C on a circulatory device, described in detail in the work [3]. Because of the corrosiveness of sulfur dioxide, the connecting hoses, the diaphragm of the circulatory pump, and the surfaces of resinous plugs were constructed of polyethylene. A gas VTI-2 analyzer was used for the analysis of the gases.

TABLE 1. COMPOSITION OF SYNTHETIC SLAGS

Slag No.	FeO, %	CaO, %	SiO_2, %	Al_2O_3, %
1	52.0	15.0	25.6	6.8
2	31.5	14.5	40.2	8.8
3	16.4	22.5	51.0	9.0

Strong sulfuric acid was used in the role of a locking liquid. It was found that the absorption of SO_2 by strong sulfuric acid for one hour at a temperature of 20°C amounts merely to tenths of one percent. Hence, the errors during the analysis of the gaseous mixture, lasting 5-7 minutes, were small. The experiments were conducted at atmospheric pressure, maintained constant by means of a special vessel made of thin polyethylene.

According to preliminary experiments, a near-equilibrium state of the mixture was achieved in 2.5-3 hours. Hence, all the experiments were carried out for 3 hours. The following sequence was followed. A porcelain tube was placed in the furnace in a horizontal position. Three crucibles with weighed amounts (8 g) of the three types of slag and metallic copper (3 g) were placed on a support inside this porcelain tube, and the tube was connected by means of hoses to the circulatory pump. The air was pumped out of the system, and then the system was filled with a given composition of the gas mixture of argon and sulfur dioxide. After that, the furnace and the circulatory pump were switched on. After completion of the experiment, a sample was withdrawn and analyzed for its content of oxygen and sulfur dioxide. The results of microscopic and chemical analyses of slags after the experiments are presented in Figures 1, 2, and 3.

It is seen from the graphs that, at a small concentration of sulfur dioxide, the content of copper in all three slags is small. This content increases with the increase of P_{SO_2}. This is

particularly noticeable in slags 1 and 2. In contrast to these slags, an increase of the copper concentration in the slag 3 is observed only after the increase of P_{SO_2} to 0.1 atm (Figure 3). After that, the content of copper in the slag slowly increases.

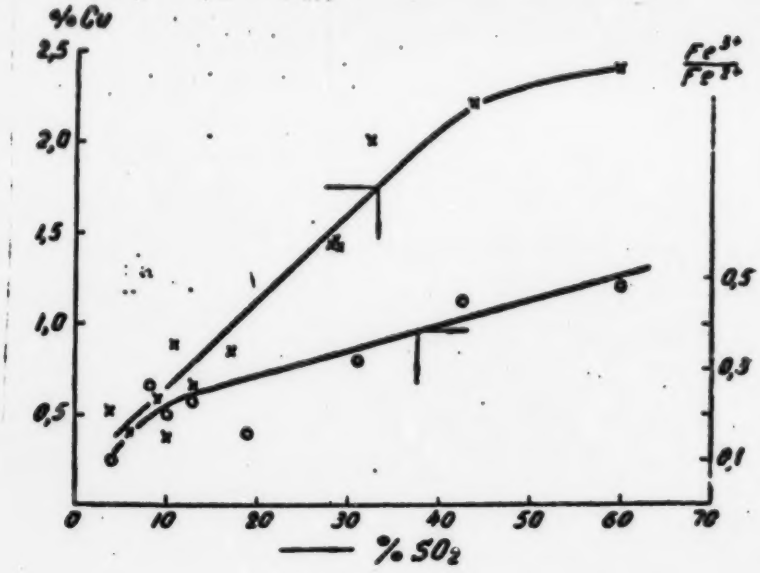

Figure 1. Dependence of the transfer of copper into slag No. 1 and the ratio $\frac{Fe^{3+}}{Fe^{2+}}$ on the concentration of sulfur dioxide in the gaseous phase.

Thus, in all the three types of slags in contact with metallic copper, and particularly in slags Nos. 1 and 2, there is a clear increase of the copper concentration with an increase of P_{SO_2}.

For a fuller clarification of this dependence, we carried out a microscopic analysis of slags obtained after the experiments. This analysis showed that, with a low content of SO_2 in the gaseous phase ($\sim$4%), the upper layer of the slag contains pyrrhotine, the middle layer contains chalcopyrite in a small amount, and there is chalcosine at the boundary between the slag and the copper.

With an increase of P_{SO_2}, we observe in the upper and middle layers of the slag a noticeable amount of magnetite as well as delafossite ($Cu_2O \cdot Fe_2O_3$), in addition to the above phases, and there is chalcosine again at the boundary between the slag and the

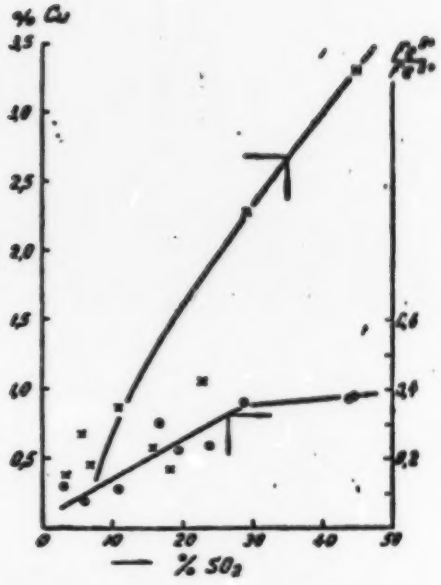

Figure 2. Dependence of the transfer of copper into slag No. 2 and the ratio $\frac{Fe^{3+}}{Fe^{2+}}$ on the concentration of sulfur dioxide in the gaseous phase.

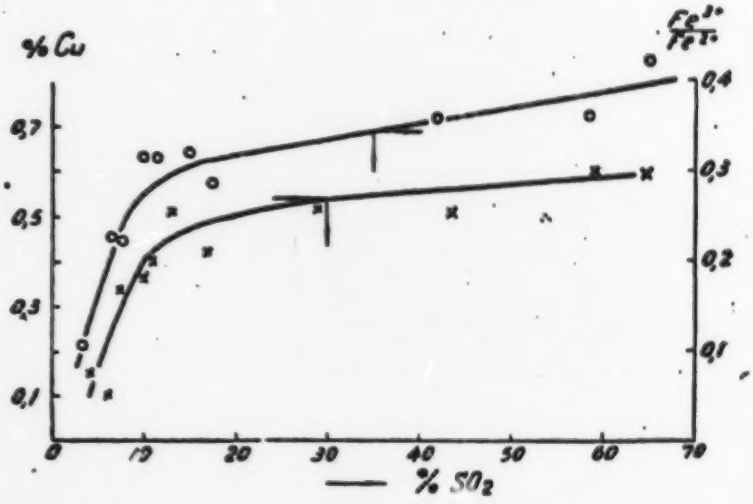

Figure 3. Dependence of the transfer of copper into slag No. 3 and the ratio $\frac{Fe^{3+}}{Fe^{2+}}$ on the concentration of sulfur dioxide in the gaseous phase.

copper. At 43% SO_2 in the gaseous phase, the picture becomes more sharply delineated, i.e., magnetite and delafossite cover a considerable part of the cross-sectional view, and chalcosine forms a continuous layer on the copper surface. The oxidized copper constitutes up to 70% of all the copper contained in the slag. For illustration,

Figure 4. Photomicrograph of slag No. 1 in contact with metallic copper, at a concentration of sulfur dioxide in the gaseous phase equal to 43.4%. Reflected light, magnification 160 X. 1 - metallic copper; 2 - chalcosine (Cu_2S); 3 - magnetite (Fe_3O_4); 4 - needles of delafossite ($Cu_2O \cdot Fe_2O_3$).

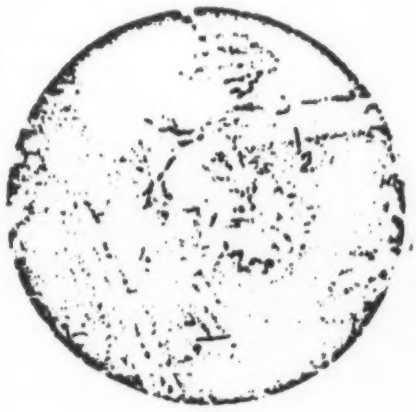

Figure 5. Photomicrograph of slag No. 1 in contact with metallic copper, at a concentration of sulfur dioxide in the gaseous phase equal to 10%. Upper layer. Reflected light, magnification 160 X. 1 - pyrrhotine (Fe_nS_m); 2 - magnetite (Fe_3O_4); 3 - chalcosine (Cu_2S); 4 - silicates.

we show in Figures 4, 5 and 6 the photomicrographs of the cross-sections of the slags under investigation. The above behavior is less pronounced for slag No. 3.

It was found by G.S. Frents [4] during an investigation of the copper - SO_2 system, that neither with a change of the partial pressure of sulfur dioxide from 0.1 to 1 atm, nor at increasing temperature from 700 to 1300°C, does copper react with sulfur dioxide. The system studied by us differed from his case only by the fact that the copper was covered with a layer of slag. The latter, apparently, facilitates the sulfurization of copper by means of sulfur dioxide. This phenomenon is confirmed, in part, by the work of German investigators [5], studying the copper - SO_2 - CO, CO_2 system. They have demonstrated that changing the CO_2/CO ratio in that system makes it possible to regulate the content of sulfur in the copper at a constant concentration of sulfur dioxide. When that ratio is high (> 1000), sulfur dioxide practically does not react with copper at all, at any partial pressure of SO_2. On the

Figure 6. Photomicrograph of slag No. 1 in contact with metallic copper, at concentration of sulfur dioxide in the gaseous phase equal to 10%. Middle layer. Reflected light, magnification 160 X. 1 - chalcopyrite ($CuFeS_2$); 2 - magnetite (Fe_3O_4); 3 - silicates.

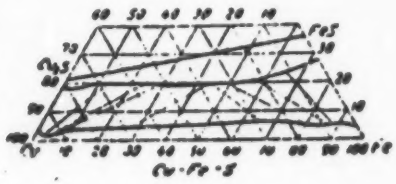

Figure 7. Phase diagram of the system Cu - Fe - S.

other hand, a decrease of that ratio is equivalent to increasing the reducing capacity of the gas, and it leads to the appearance of sulfur in copper.

In our case, the role of the reducing agent was played by the iron oxide in the slag. The results of microscopic analysis of the layers of slag suggest that the sulfurization of copper proceeded in the following stages. At first, sulfur dioxide reacted with iron oxide in the surface layer of the slag according to reaction (1)

$$10FeO\ (slag) + SO_2 = 3Fe_3O_4 + FeS. \qquad (1)$$

The iron sulfide formed in this reaction diffused to the surface of copper and sulfurized it:

$$FeS + 2Cu = Cu_2S + Fe. \qquad (2)$$

The metallic iron formed was dissolved in copper and partly, maintaining the equilibrium state, reduced the magnetite to iron oxide. However, if we examine the balance of oxidation of the iron oxide by sulfur dioxide to magnetite in accordance with reaction (1) and its reduction by metallic iron

$$Fe_3O_4 + Fe = 4FeO, \quad (3)$$

then it will become obvious that the oxidation of the slag $\left(\frac{\%Fe^{3+}}{\%Fe^{2+}}\right)$ increases with an increase in the system of the partial pressure of sulfur dioxide.

These conclusions are corroborated by the results of experiments (Figure 4, 5, 6).

Another variant of the appearance of the oxide and sulfide of copper in the slag is possible. During the oxidation of metallic copper by magnetite, the first product could be copper oxide, which then could interact with troilite according to the exchange reaction (4)

$$Cu_2O + FeS = Cu_2S + FeO. \quad (4)$$

Consequently, irrespective of the order and course of reactions for the formation of copper oxide and sulfide, one can reach the following conclusion: with the presence of metallic copper, its sulfide, and magnetite in the slag copper oxide should appear according to reaction (5)

$$\begin{array}{l} 2Cu + Fe_3O_4 = Cu_2O + 3FeO, \\ 2Cu_2O + Cu_2S = 6Cu + SO_2 \\ \hline Fe_3O_4 + Cu_2O + Cu_2S = 3FeO + SO_2 + 4Cu \end{array} \quad (5)$$

As is seen from equations of reaction (5), the concentration of copper oxide in the slag will be higher, the larger is the activity of copper, iron oxide in the slag, and P_{SO_2}.

We must now consider the activity of copper. In experiments carried out on the white matte - slag - SO_2 system, which employed analogous compositions of slags, no increase in the content of copper was observed. On that basis, the conclusion was made that the activity of copper in mattes, including white matte, is of little importance. Another dependence is observed in the case where metallic copper is in contact with the sulfide phase. Then, the activity of copper increases to such an extent that oxidized

copper, being in equilibrium with its sulfide, appears in the slag. This behavior is explained by the fact that the activity of copper in both phases (in copper and matte phases) is equal. The copper phase, in such a case, is close to the composition of blister copper, defined by the phase diagram of the system Cu - Fe - S, shown in Figure 7 [6]. It follows from this diagram that the copper phase of matte separated into layers has nearly one and the same composition (from 80 to 50% copper). This is explained by the fact that, in the region of separation into layers, the fan-shaped lines converge into a cluster in the copper corner.

Thus, the activity of copper in the copper - matte system is close to unity. Therefore, the concentration of copper in oxide form in the slag is determined here only by the partial pressure of SO_2 and composition of the slag, inasmuch as the activity of copper will be constant and close to unity, irrespective of the composition of rich matte present over the copper phase. Calculations of the copper content in the form of Cu_2O in the slag as a function of P_{SO_2}, carried out in the work [2], are nearly in full agreement with the experimentally obtained results.

Conclusions

1. Interaction of sulfur dioxide with metallic copper, with the formation of the sulfide and copper oxide, is possible in the presence of a slag containing iron oxide.

2. In the smelting of copper concentrate directly into blister copper, it is not possible to obtain this blister copper without the matte phase and slag free from copper oxide. The concentration of copper oxide will depend on P_{SO_2} and composition of slag, and will barely depend on the composition of the intermediate matte phase (this conclusion is valid under the condition that the system does not contain free oxygen).

3. The concentration of the oxidized copper in the slag, all other conditions being equal, mentioned above, decreases with the

transition from ferrous to highly siliceous slags.

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